# Polycyclic aromatic hydrocarbons (PAHs) at High Mountain Site in North China: Concentration, source and health risk assessment

**Jing Liu[1], Yan Wang[2], Peng-hui Li[1*],You-ping Shou[3*], Tao Li[2],Min-min Yang[2], Lei Wang[4], Jun-Jie Yue[1], Xian-liang Yi[5], Li-Qiong Guo[6]**

*[1] School of Environmental Science and Safety Engineering, Tianjin University of Technology, Tianjin, 300384, China*

*[2] School of Environmental Science and Engineering, Shandong University, Jinan, 250100, China*

*[3]Key Laboratory of Environmental Protection Technology on Water Transport, Minist ry of Transport, Tianjin Research Institute for Water Transport Engineering, Tianjin, 300384, China*

*[4]Hebei Geological Laboratory,Hebei,071051,China*

*[5]School of Food and Environment, Dalian University of Technology, Panjin, 124221, China;*

*[6]Department of Occupational & Environmental Health, School of Public Health, Tianjin Medical University, Tianjin, 300070, China*



## Abstract

Polycyclic aromatic hydrocarbons (PAHs) in fine particulate matter ($PM_{2.5}$) samples were analyzed at the top of Mount Tai in northern China from June to August of 2015. The mean concentration of $PM_{2.5}$ was 54.94 μg $m^{-3}$(10 - 126 μg $m^{-3}$), and the mean concentration of PM2.5-bound PAHs was 1.359 ng $m^{-3}$ (0.296 - 5.349 ng $m^{-3}$). Phe, Flu and IcdP were the three most abundant PAH species, with a mean concentration of 0.331, 0.128 and 0.100 ng $m^{-3}$, respectively. Particle phase organics were scavenged at the early stage of cloud/fog event, which cause a clear decrease in PAHs concentration. However, the concentration of PAHs increased after cloud/fog

∗Corresponding author:Peng-hui Li,Tel/Fax: 86 22 60214185; E-mail:lipenghui406@163.com

∗Corresponding author:You-ping Shou,Tel: 022-59812345; Tax:022-59812389

E-mail: syp851228@126.com

events since the liquid phase organics in clouds could be absorbed by particle phase organics. The results of PAHs levels used potential source contribution function, diagnostic ratio and principal component analysis suggested that significant contributions regions of PAHs at Mount Tai are the north (Hebei Province) and southeast (Henan Province) directions. Furthermore, vehicular emission, coal combustion and biomass combustion were the possible emission sources of PAHs. The estimated inhalation incremental lifetime cancer risk (ILCR) of three groups (Infants, Children, Adults) were less than $1\times10^{-6}$, with mean values of $2.58\times10^{-9}$, $2.05\times10^{-8}$ and $4.86\times10^{-8}$, respectively, suggesting the baseline of inhalation exposure values are acceptable in this present study.

**Key words**: $PM_{2.5}$; PAHs; concentration; source; risk assessment

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class group of complex organic compounds containing hydrogen and carbon and constituted fused ring structure including at least two linear or cluster benzene rings (Pongpiachan, 2016; Lai et al., 2017). PAHs originated from both natural (i.e., forest fires, volcanic eruptions and etc.) and anthropogenic sources (i.e., industrial production, rubbish incineration, vehicle emission and etc.) (Kamal et al., 2016). PAHs are widely distributed in atmosphere (Liu et al., 2016), and they can pose adverse health effects to human beings because of their well-known carcinogenic, mutagenic and teratogenic properties (Hussain et al., 2016; Bhargava et al., 2004). For example, exposure to PAHs and their secondary metabolites may changes in the original sequence of the DNA, which cause DNA

mutation, and lead to increased human health risks (Kelly et al., 2007; Li et al., 2016c; Wilcke, 2007). Therefore, PAHs in various environmental and biological compartments have been extensively studied in recent years (Gong et al., 2011; Sharma et al., 2007).

PAHs' existence in the natural atmosphere can be in both vapour and particle phases (Zhang et al., 2015; Wang et al., 2013). Generally, PAHs in low molecular weight (LMW; 2-3 rings) are potentially to be more concentrated in gas-phase while the contribution of particle phase was very important to the higher molecular weight (HMW;4-6 rings) (Li et al., 2016b). HMW PAHs have been suggested to be more mutagenic and carcinogenic than LMW PAHs (Li et al., 2010). Up to date, a lot of studies have been done to study the PAH concentrations in the cities in both eastern and western countries (Hoseini et al., 2016).

Studies on PAHs concentration and their sources at remote areas, especially at high mountain sites far away from anthropogenic pollution sources, can provide valuable information on sources and atmospheric processing of air pollutions. Nevertheless, few studies have been done to elucidate these issues. Therefore, in this study, sampling site was set up atop Mount Tai, which is a regional background site and can reflect the basic pollution status of the free troposphere. The aims of this study were to: (1) investigate concentrations of PAHs and the variation of the PAH concentrations during cloud/fog event in Mount Tai; (2) investigate potential source by applying potential source contribution function (PSCF), principal component analysis (PCA) and diagnostic ratios (DR) and (3) assess the incremental lifetime

cancer risk (ILCR) of PAHs.

## 2 Materials and methods

### 2.1 Sampling sites

Mount Tai, as a popular tourist attraction in China, and is impervious to most industrial pollutions. It is located in north Tai'an City in the middle of Shandong Province in the north of China, and the distance from Atlantic Ocean is 230 km (Figure 1). The annual average daily temperature here is about 7 degrees Celsius(°C), and the average elevation is 1532.7 m. The monitoring site of the present study is located in a meteorological station at the summit of Mount Tai (117°06′ E, 36°16′ N), which was established in 1932.

**Figure 1**

### 2.2. Sample collection

There are totally 75 $PM_{2.5}$ samples were collected at the monitoring station from June to August, 2015. These samples were incessantly collected onto quartz filters (203×254mm, Munktell, Sweden) using high-volume samplers (HI-Q 7386, manufactured by Environmental Products Company, INC. San Diego, CA, USA), which was operated at a flow rate of 1000 L/min with a 2.5-μm cut-point for $PM_{2.5}$ (D50=2.5 ± 0.2 μm). After sampling, all of the quartz filters were packed with aluminum foil and stored at −20 °C. All the sample analyses were finished within two weeks after sampling.

### 2.3. Sample extraction and analysis

The detailed procedures for sample extraction and analysis have been described

elsewhere (Li et al., 2010). Briefly, the pall quartz fiber filters used to collect the samples were extracted using Accelerated Solvent Exarator (DIONEX ASE 300) to enrich PAHs. The PAHs was eluted with 33 ml n-hexane/acetone solvents in the ratio of 1:1 and the eluate were concentrated to 1 mL with nitrogen stream. The samples which had been eluted were then analyzed with Gas chromatography with mass selective detection (SHIMADZU 2010plus). The detection device was provided with a 60 m DB-5 ms capillary column which was operated in the electron impact mode (70 eV). A series of heating were performed. In the end, the solvent of 1 mL was analyzed with an Agilent 7890B-5977A GC-MS (Agilent Technologies, Santa Clara, CA, USA) to conduct data acquisition and identify the chromatographic peaks of samples.

## 2.4. Quality control

All samples must pass through stringent quality assurance. In sampling, field blanks were collected to identify the background contamination. In addition, method blanks (solvent only) as well as spiked samples were conducted simultaneously. PAHs were not able to be detected in these blanks. To evaluate the procedural performance and matric effects, surrogate standards were applied to the whole samples which include quality assurance samples. A total of 17 priority PAH species were analyzed in the present study, including Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flo), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flu), Benz[a]anthracene (BaA), Chrysene (Chr), Pyrene (Pyr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Benzo[e]pyrene (BeP),

Dibenz[a,h]anthracene (DahA), Indeno[1,2,3-c,d]pyrene (IcdP), Benzo[ghi]perylene (BghiP), Coronene (Cor). The overall recovery rate of the analyses by applied technique and method were from 64% to 92%.

# 3 Results and discussion

## 3.1 $PM_{2.5}$ and PAH concentration levels

### 3.1.1 The concentration of $PM_{2.5}$

The daily concentrations of $PM_{2.5}$ in ambient air from June to August of 2015 ranged from 10 to 126 μg $m^{-3}$, with a mean concentration of 54.94 μg $m^{-3}$ (Figure 2). These $PM_{2.5}$ levels substantially fell into the Class 2 of $PM_{2.5}$ standard in China, which is 75.0 μg $m^{-3}$. Nevertheless, during the sampling period, the contribution of anthropogenic emissions was considered to be low and higher mass concentrations of $PM_{2.5}$ may happen on colder days at the Mount Tai because nearby residents need more energy for heating in winter.

**Figure 2**

### 3.1.2 Levels of pollutant concentrations

The PAH concentrations in $PM_{2.5}$ samples were illustrated in Table1 and total PAHs in $PM_{2.5}$ was 1.359 ng $m^{-3}$, ranging from 0.296 to 5.349 ng $m^{-3}$. Phe was the most abundant PAH species, with a mean concentration of 0.331 ng $m^{-3}$(0.004 to 2.098 ng $m^{-3}$). Flu and IcdP were the second and third most abundant PAH compounds, with mean concentrations of 0.128 (0.023 to 0.469 ng $m^{-3}$) and 0.100 ng $m^{-3}$ (0.011 to 0.278 ng $m^{-3}$), respectively. The other PAHs species accounted for less than 6% of the total PAHs. The mean concentrations of the six individual PAHs with

the most large amount in $PM_{2.5}$ have the decreasing order of Phe (mean 0.331 ng $m^{-3}$) > Flu (mean 0.128 ng $m^{-3}$) > IcdP (mean 0.100 ng $m^{-3}$) > BghiP (mean 0.096 ng $m^{-3}$) > BeP (mean 0.096 ng $m^{-3}$) > BbF (mean 0.092 ng $m^{-3}$).

Compared with PAH concentrations in the same site reported by previous studies, the concentration of the total PAHs at Mount Tai in this study was only about one fifth of that reported previously (i.e., 6.88 ng $m^{-3}$) (Li et al., 2010). This decreasing trend of PAHs pollutions is probably because the Chinese government has been committed to routine monitoring of air quality and put many efforts into improving it. Compared with those in other mountains or background sites, PAH concentrations at Mount Tai are much lower. For example, the total PAH concentrations in Gosan, South Korea, Mount Lu, and Yellow River Delta National Nature Reserve were reported to be 4.299, 18.30, and 7.43 ng $m^{-3}$, respectively (Kim et al., 2012; Li et al., 2016a; Zhu et al., 2014). Besides the difference in total PAH concentration, PAH compositions vary between different sampling sites. For example, in this study, Phe and Flu were the two most abundant PAH species, which accounted for nearly 30% of the total PAH concentration. Unlikely, Pyr and Phe accounted for the largest percentage (>29%) among all the PAH species in Mount Lu (Li et al., 2016a), and BghiP and BbF in Gosan, South Korea were the most abundant (>28%; Kim et al., 2012).

**Table 1**

Cloud/fog event was recorded during the sampling period. Thus, PAH concentrations in $PM_{2.5}$ samples were analyzed during this event to determine their fluctuation under different meteorological conditions. Cloud/fog may have a very

complicate impact on particles aerosols. A significant decrease in PAH concentrations could be observed during this meteorological phenomena as the organic pollutants in particles aerosols in the atmosphere could be scavenged remarkably (Wang et al., 2015). In the present study, four PAH species (i.e, BghiP, BaP, BbF and Cor) were chosen to analyze the variation of PAH concentrations during the cloud/fog event. The results showed that the concentrations of these four PAH species declined continuously at the beginning of the event, but increased after the event (Figure 3). PAHs were scavenged at the early stages of cloud/fog event which resulted in a decrease of the PAH concentrations. When cloud/fog dissipates gradually, the abundant liquid phase organic pollutant in clouds could be absorbed by particle phase organic pollutant, leading to a rapid increase of the particle phase organic pollutant mass concentration, thereby increasing the PAH concentrations after the cloud/fog event (Li et al., 2015a).

**Figure 3**

## 3.2 Identification of PAH sources

### 3.2.1 Contributions of Regional Sources

To analyze the potential source regions and pathways of PAHs at Mount Tai, 24-h backward trajectories were used in potential source contribution function (PSCF) analysis. Figs.4 (a-e) shows the distinctive potential source region distributions for individual PAH in $PM_{2.5}$ at Mount Tai. BaP, Flu, Ant, Phe and Flo exhibited similar source region distributions. The highest PSCF values were all found to the north of Mount Tai (Hebei Province). Furthermore, BaP also has high values in the southwest

of Mount Tai (Henan Province), indicated that these areas were very significant source regions for these pollutants. In Hebei and Henan Province, biomass and coal combustion were the dominant mixed sources for the local PAHs emission (Wu et al., 2015;Wu et al., 2016).

**Figure 4**

Overall, the north (Hebei Province) and southeast (Henan Province) directions were probably the important source regions of PAHs at Mount Tai. Some appropriate effective measures should be taken to reduce the PAHs concentration in these regions.

### 3.2.2 Contributions of Emission Sources

The PAH diagnostic rate has recently been used to identify and validate the source of pollution emissions (Li et al., 2016d). In present study, several diagnostic ratios, including Phe/ (Phe + Ant), Flu/ (Flu + Pyr), BaA/ (BaA + Chr) and IcdP/ (IcdP + BghiP) were introduced to analyze the potential sources of PAHs detected at Mount Tai.

This ratio of Phe/ (Phe + Ant) could be used as a source indicator that potentially from petrogenic hydrocarbons (<0.7) or the biomass burnings (>0.7) (Sienra et al., 2005; Alves et al., 2001). The ratio of Phe/(Phe + Ant) in the present study was 0.88 (Table 3), which indicate the biomass combustion could be the major source of PAH pollutions detected in Mount Tai area.

As for the diagnostic ratio of Flu/(Flu + Pyr), a value smaller than 0.4 implied unburned petroleum as the main source of PAH pollutions; the value between 0.4 and 0.5 indicated the sources from liquid fossil fuel; and the value larger than 0.5

suggested the sources might be potentially from wood and coal (Yang et al., 2017). In this study, the ratio of Flu/ (Flu + Pyr) in Mount Tai was 0.63 (Table 2), which indicate a significant contribution from coal and wood combustion in this area.

Tobiszewski and Namiesnik (2012) reported that the ratio of BaA/ (BaA + Chr) between 0.2 and 0.35 demonstrated the coal combustion sources of PAHs, and the ratio > 0.35 suggested the vehicular emission sources. Therefore, in Mount Tai, coal combustion may be the important source of PAHs in particles as the ratio of BaA/ (BaA + Chr) was 0.33 (Table 2).

The ratio of IcdP/ (IcdP +BghiP) has been widely used as an source indicator as well. A ratio < 0.2 reflected the petrogenic sources; a ratio between 0.2 and 0.5 implied the petroleum combustion sources (liquid fossil fuel, vehicle, and crude oil combustion); and a ratio >0.5 suggested the combustion sources from wood and coal (Yunker et al., 2002). The value of this in study was 0.51, indicating the comprehensive contributions from the coal and wood combustion sources.

**Table 2**

Because Mount Tai is a high altitude background site, the results of the present study can well reflect an overall picture of possible PAH sources in China. The above study reflected the advantage of both coal and biomass combustion in contributing to the PAH pollutions in particle samples collected at Mount Tai, which suggested that the dominant energy sources were still supplied by coal combustion in China. It should be noted that these diagnostic ratios might be affected by many factors, thus they could only offer general qualitative information on pollutant sources. For

example, PAHs can react with many other compounds (i.e, hydroxyl radicals) in the atmosphere, resulting in altered diagnostic ratios values. Besides, degradation during the transport can also affect the diagnostic ratios of PAHs (Li et al., 2015b). Therefore, in addition to these diagnostic ratios, principal component analysis (PCA) was applied to quantify thesources of pollutants and make complementary explanations. In the PCA results, factors with eigenvalue >1 were considered (Table 3).

Three factors accounted for 86.7% of the total variance of the data. Factor 1, which explained31.4% of the variance, had high loading on Ant, Flo, Ace, Phe and Flu. Because these four PAH species mainly originated from coal combustion, factor 1 was considered as indicative of coal combustion sources (Zhang et al., 2008). Factor 2, explaining 30.8% of the variance, illuminated high loading on BghiP, Chr, BeP and DahA. The presence of BghiP and Chr could point to industry emissions source (Ravindra et al., 2006). DahA was originated from different sources, and BeP indicated stationary emission sources (Zhang et al., 2008). Therefore, factor 2 could be regarded as an indicative of multiple sources. Factor 3 showed high loadings on IcdP, BbF, BaA, Pyr and BkF, and it accounted for 24.6% of the variance. The presence of IcdP, BbF, BaA and Pyr were considered the major component of gasoline-powered emission. BkF was used as a special source indicator of diesel-powered emissions (Guo et al., 2003; Li et al., 2016). Therefore, factor 3 suggested pollution sources from vehicular emission.

**Table 3**

From the overall PCA results, it appeared that coal combustion, vehicular

emission and industrial emission were the main sources of PAH pollution at Mount Tai. Regarding the reactivity and degradation of different PAH species, more efforts should be made to further understand the profile of PAH sources.

## 3.3 Risk assessment

Making use of the background PAHs concentrations at Mount Tai, we calculated the baseline of inhalation exposure values for public health. In order to assess the cancer risk attributed to carcinogens, the incremental lifetime cancer risk (ILCR) was analyzed, which was expressed as the lifetime average daily dose (LADD) multiplied by the BaP slope factor. Besides, the cumulative probability of the total risk were also evaluated by means of Monte Carlo simulation. Lifetime was divided into three groups according to age (infants: 0-1 years, children: 2-18 years and adults: 19-70 years). The total LADD is the sum of the LADD values of the above three age groups. The equations used to estimate LADD and ILCR are listed as follows:

$$LADD = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

$$ILCR = LADD \times \left\{ CSF \times \left(\frac{BW}{70}\right)^{\frac{1}{3}} \right\} \times cf$$

where C is the background equivalent concentration (BEC), which is calculated using the method described in (Jung et al., 2010). The carcinogenic risk of a PAH mixture can be expressed by its total $BaP_{eq}$ concentration (BEC), which is expressed as BEC = $\sum C_i \times TEF_i$, where $TEF_i$ is the toxicity equivalency factor of PAH congener (Tiwari et al., 2015). The $TEF_i$ values for Ace, Acy, Flo, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, BeP, DahA, IcdP, BghiP and Cor were listed in Table 4, which were achieved

272 from (Liu et al., 2015).

273 **Table 4**

274 The meaning and value of the other parameters used for analysis in the equations were
275 derived and presented in Table 5.

276 **Table 5**

277 An ILCR value of $1\times10^{-6}$ was defined to be inconsequential or "essentially
278 negligible" since this risk level is comparable as that of some normal human activities
279 such as diagnostic X-rays and fishing (Huang et al., 2016). An ILCR value between 1
280 $\times10^{-6}$ and 1 x $10^{-4}$ was regarded acceptable, and a greater value ($>1\times 10^{-4}$) was
281 considered serious (Peng et al., 2011). The probability density of the present study of
282 ILCR is illustrated in Fig.5. The median values of inhalation risk from three groups
283 (Infants, Children, Adults) were estimated to be $1.53\times10^{-9}$, $1.11\times10^{-8}$ and $2.57\times10^{-8}$,
284 respectively, and the mean values of inhalation risk from all the three groups were
285 estimated to be in the range of $2.58\times10^{-9}$- $4.87\times10^{-8}$. Both ILCR values decreased in
286 the following order: adults > children > infants, and the ILCR values were less than
287 $1\times10^{-6}$, suggesting exposure to PAHs posed an acceptable potential cancer risk in
288 Mount Tai in this study. However, this level can only reflect the baseline of the region.
289 The real risk values may otherwise be underestimated. In many urban areas of China,
290 various local emission sources would contribute more polycyclic aromatic
291 hydrocarbons, which increase the lung cancer risks and the health risk was relative
292 high in these regions (Huang et al., 2016; Li et al., 2013; Liu et al., 2015). Therefore,
293 further health risk assessment needs to be done in urban areas.

**Figure 5**

## 4 Conclusion

Fine particle phase PAH concentrations were investigated from June to August of 2015 at Mount Tai, which can perform as a background region in Northern China. $PM_{2.5}$ concentrations during this observation period ranged from 10 to 125μg $m^{-3}$, with a mean concentration of 54.94 μg $m^{-3}$. The total PAHs concentrations ranged from 0.296 to 5.349 ng $m^{-3}$, with a mean concentration of 1.359 ng $m^{-3}$, and Phe was the most abundant PAH species, with a mean concentration of 0.331ng $m^{-3}$. PAHs concentration decrease remarkably at the beginning of cloud/fog event because of certain capacity of scavenging PAHs by cloud/fog, while the concentration of PAHs increased continually when cloud/fog dissipated gradually since the liquid phase PAHs could be absorbed by particle phase organic pollutant. The results of DR、PCA and PSCF analysis suggested the north (Hebei Province) and southeast (Henan) areas are the major source regions of PAHs at Mount Tai. In these regions, PAHs concentrations were contributed from coal combustion, biomass combustion and vehicle emissions, which are primary inputs to ambient PAHs at Mount Tai due to long-range transport of air masses. The ILCR values of cancer risk assessment from three groups (Infants, Children, Adults) were estimated to be in the range of $2.58\times10^{-9}$- $4.87\times10^{-8}$. All of values were less than $1\times10^{-6}$, suggesting the level of cancer risk in Mount Tai is acceptable during the sampling period of the present study. However, since most of the parameters were applied from USEPA and these data may be different in China for ethnicity differences, some uncertainties could be existed in

316 the risk assessment result. In addition, this result of this present study can only reflect
317 the baseline risk level of the region, population might be exposed to various sources
318 of local emission, and the real health risk would be enhanced. Therefore, further
319 research need to be done in the future.

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472

## Figure Captions

**Figure 1**: Location of our site at the summit of Mount Tai

**Figure 2**: Mass concentrations of $PM_{2.5}$ ($\mu g\ m^{-3}$).

**Figure 3**: The variation of four PAH species (i.e, BghiP, BaP, BbF and Cor) concentrations during the cloud/fog event.

**Figure 4**: Likely source regions of (a) BaP, (b) Flu, (c) Ant, (d) Phe and (e) Flo identified via PSCF plots during the sampling period.

**Figure 5**: Cumulative probability of incremental lifetime cancer risk (ILCR) from inhalation exposure to PAH in $PM_{2.5}$ by the general population ((a) Infants, (b) Children and (c) Adults).

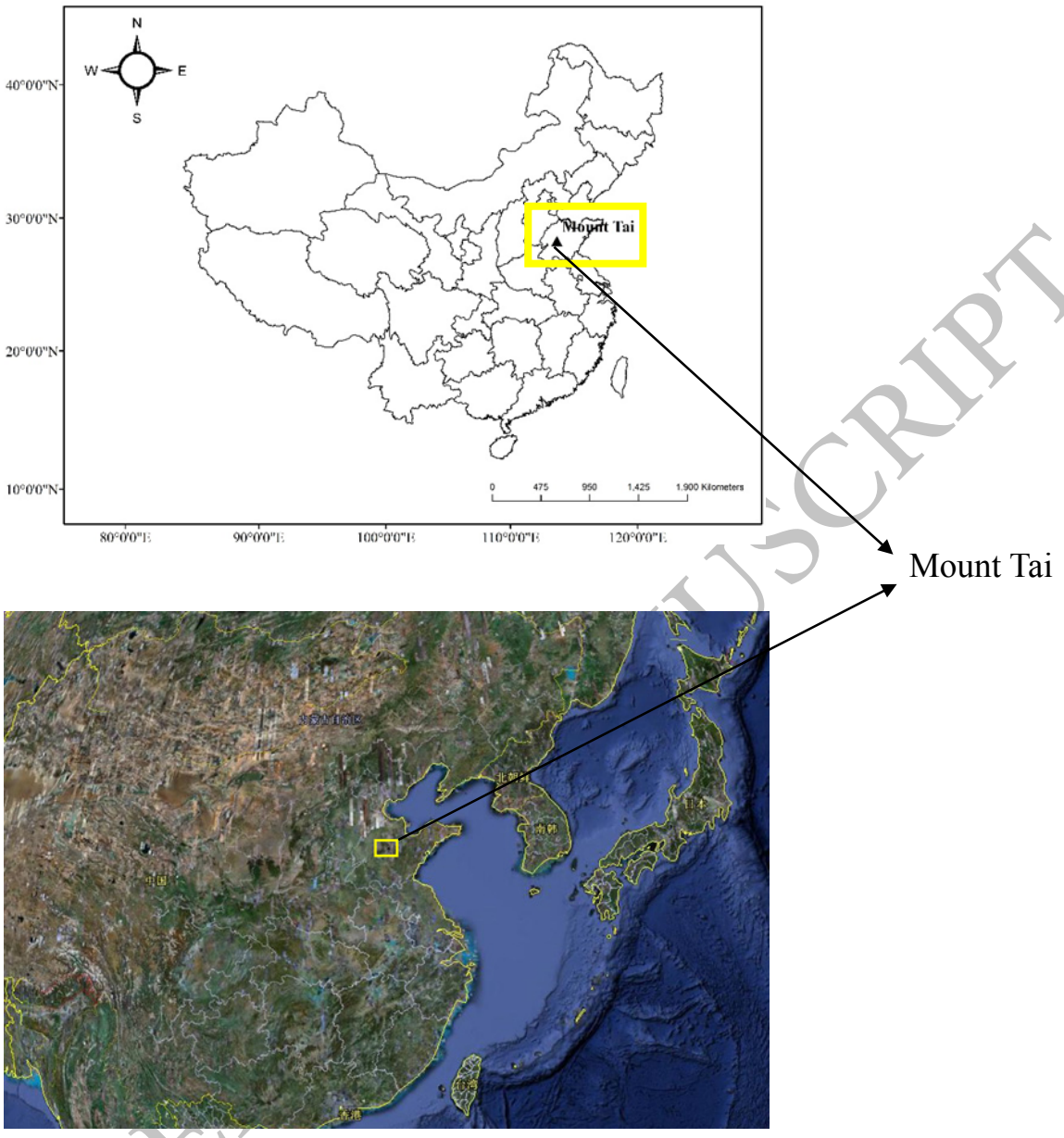
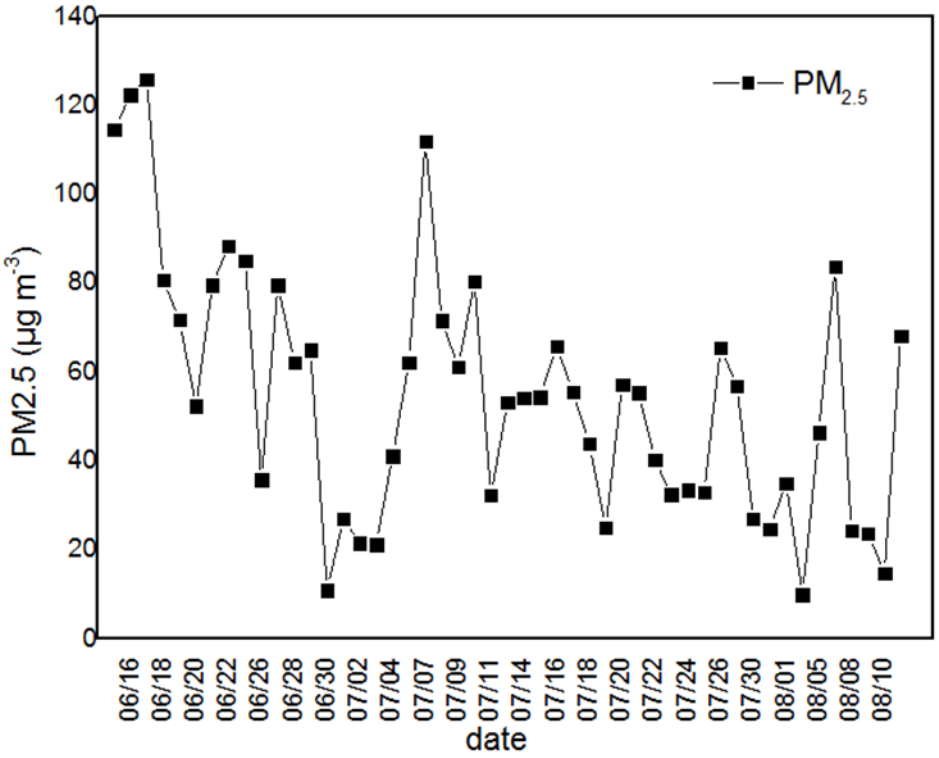



**Fig. 1**.

490

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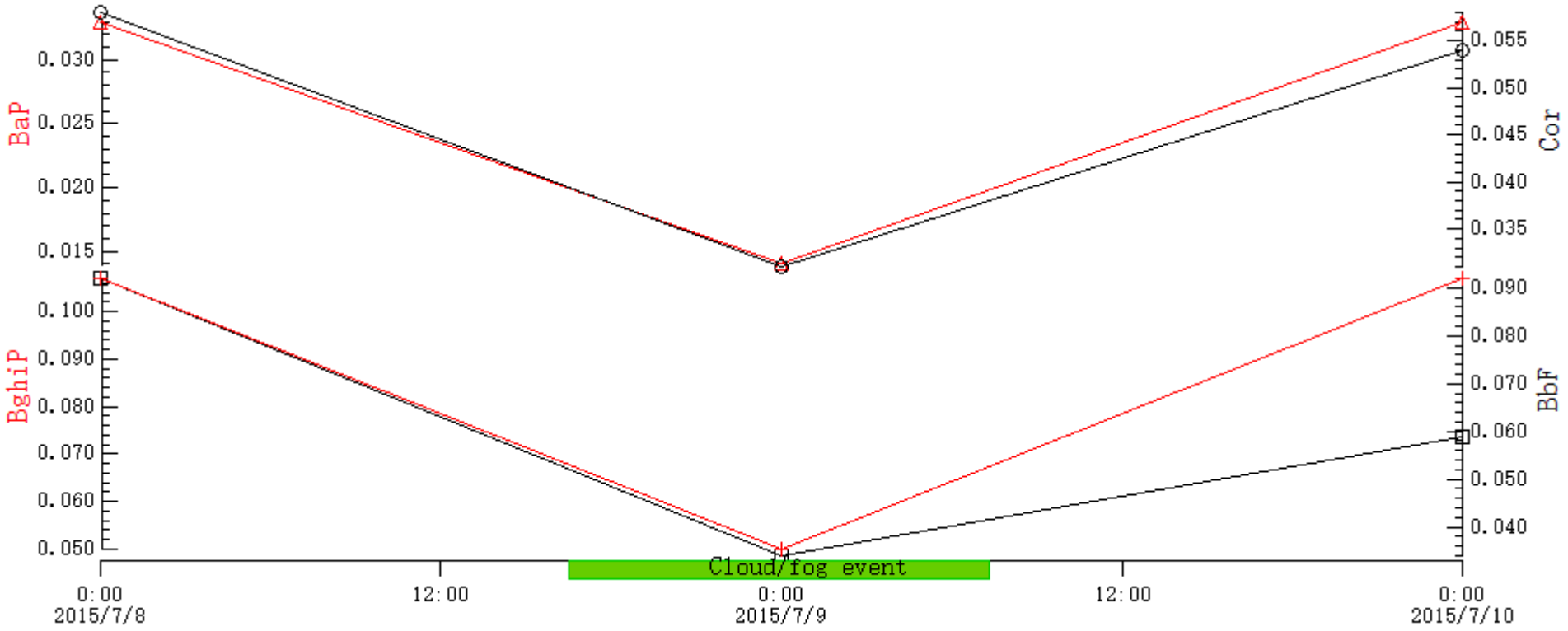
492 **Fig. 2.**

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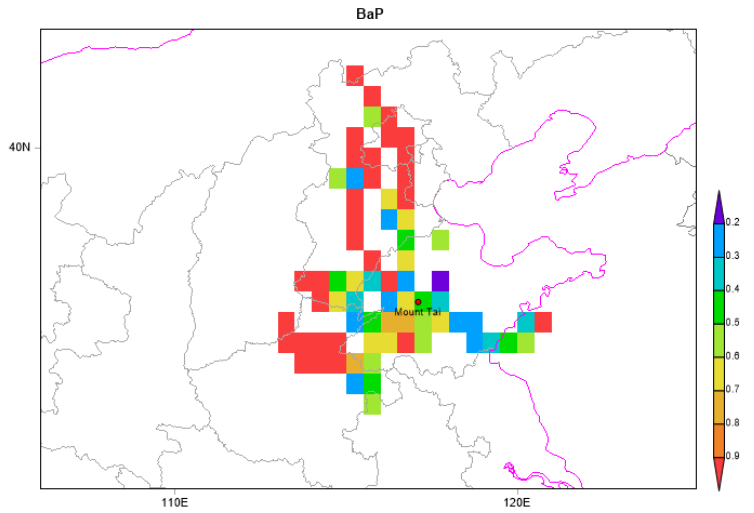
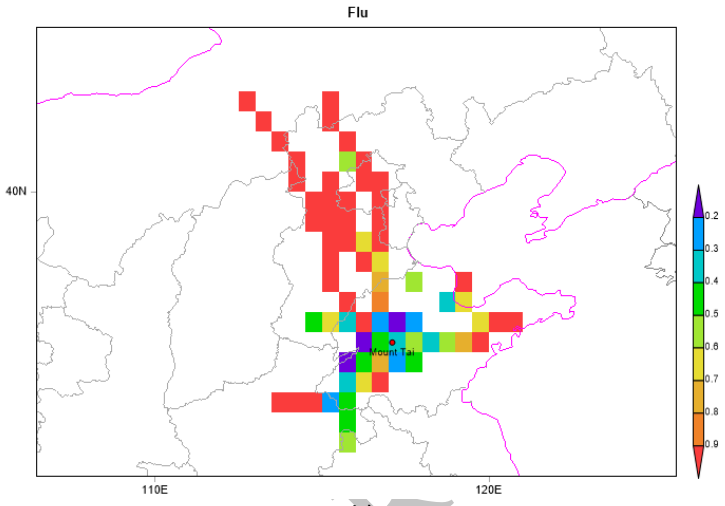
494

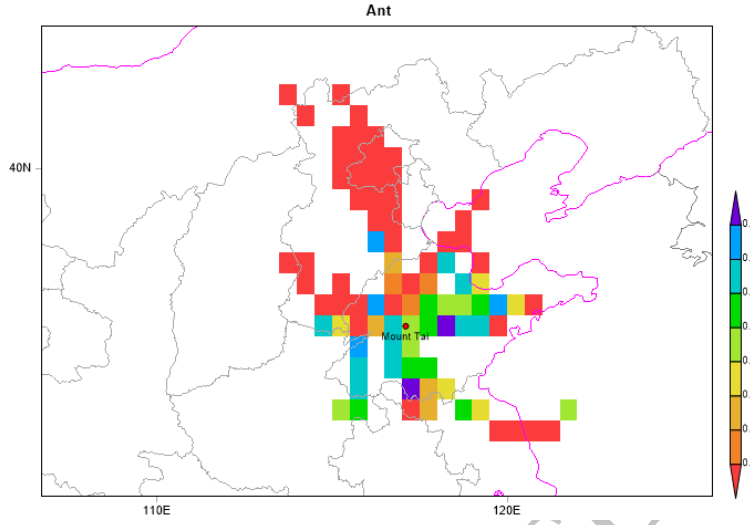
**Fig. 3.**


BaP
40N
110E
120E
Mount Tai
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

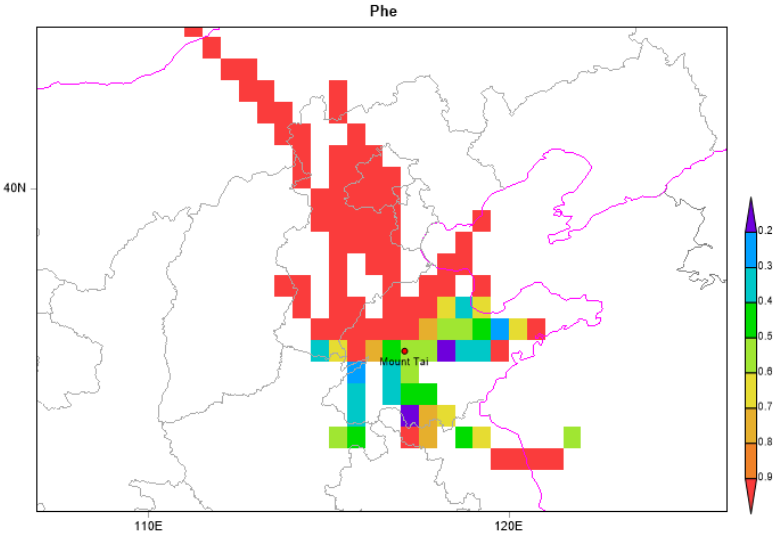
a)


Flu
40N
110E
120E
Mount Tai
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

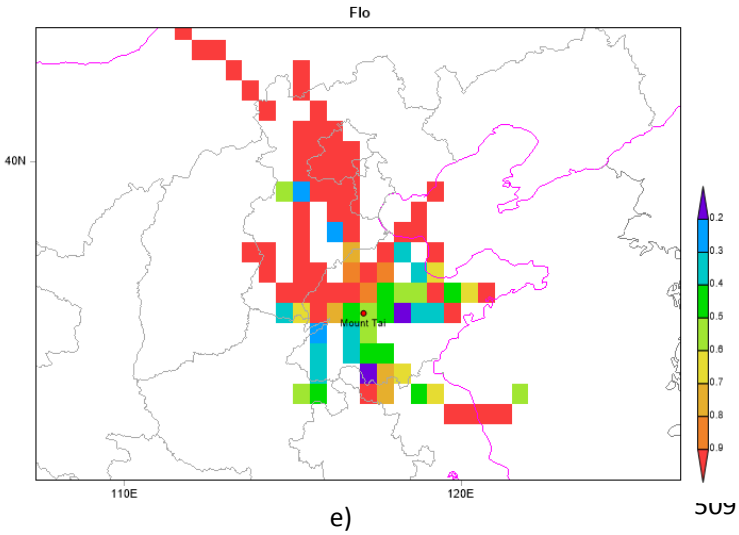
b)


Ant
40N
110E
120E
Mount Tai

c)

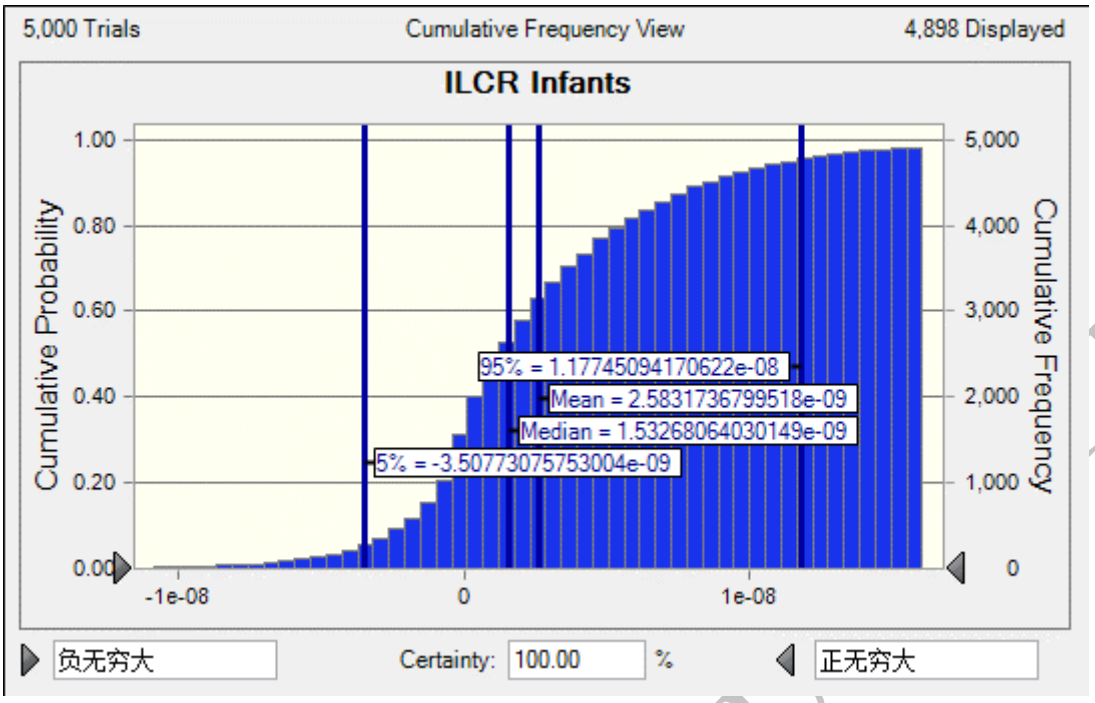

Phe
40N
110E
120E
Mount Tai
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

d)

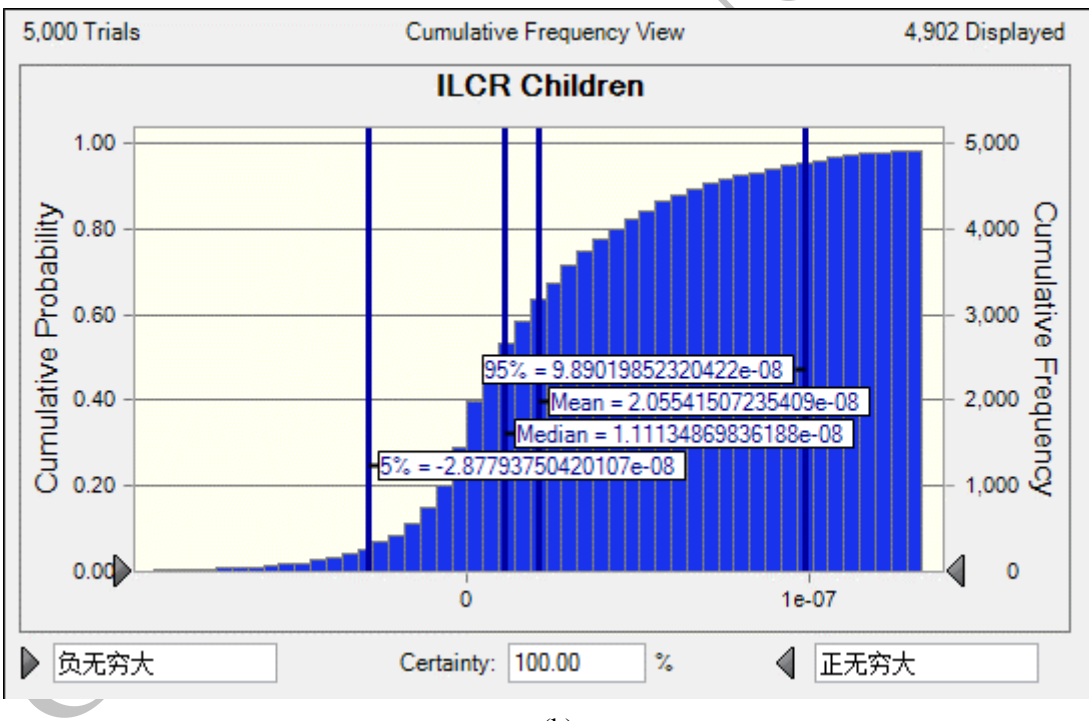

Flo
40N
110E
120E
Mount Tai
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

e)

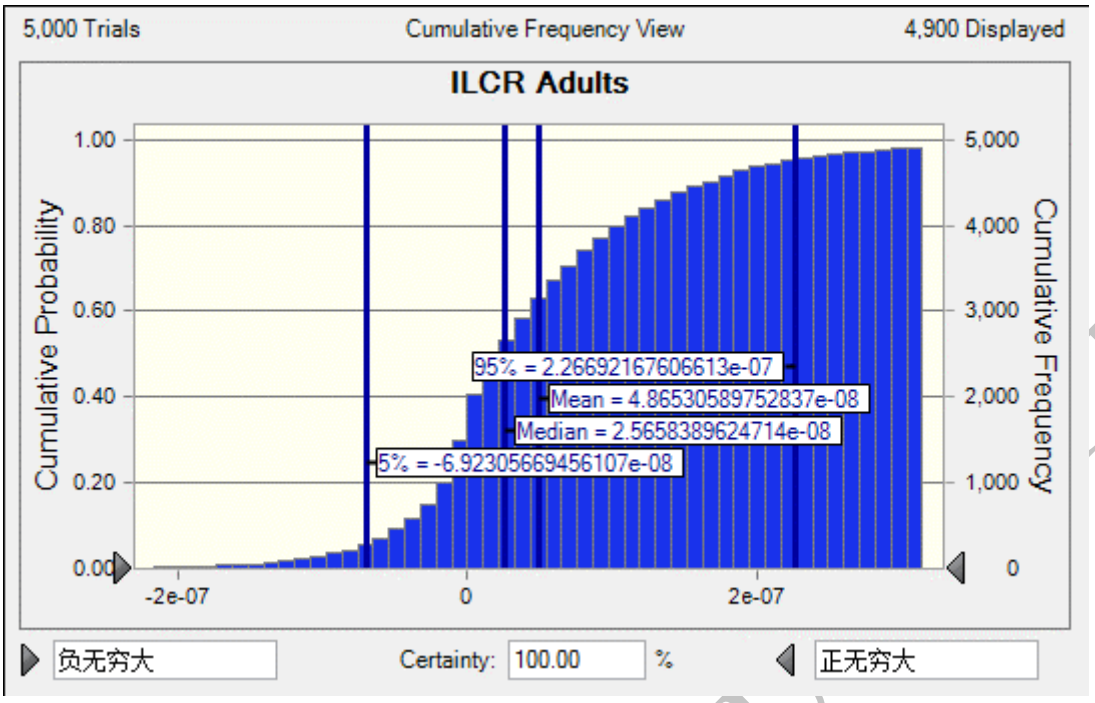
**Fig. 4.**


5,000 Trials
Cumulative Frequency View
4,898 Displayed
ILCR Infants
Cumulative Probability
Cumulative Frequency
1.00
0.80
0.60
0.40
0.20
0.00
5,000
4,000
3,000
2,000
1,000
0
95% = 1.17745094170622e-08
Mean = 2.5831736799518e-09
Median = 1.53268064030149e-09
5% = -3.50773075753004e-09
-1e-08
0
1e-08
负无穷大
Certainty: 100.00 %
正无穷大

(a)


5,000 Trials
Cumulative Frequency View
4,902 Displayed
ILCR Children
Cumulative Probability
Cumulative Frequency
1.00
0.80
0.60
0.40
0.20
0.00
5,000
4,000
3,000
2,000
1,000
0
95% = 9.89019852320422e-08
Mean = 2.05541507235409e-08
Median = 1.11134869836188e-08
5% = -2.87793750420107e-08
0
1e-07
负无穷大
Certainty: 100.00 %
正无穷大

(b)




(c)

**Fig. 5.**

519 **Table Captions**

520 **Table 1**: Total PAH Concentrations (Mean (Minimum-Maximum), ng $m^{-3}$) at Mount Tai and Other

521 Study sites During the Sampling Period.

522 **Table 2**: Diagnostic PAH ratios for samples collected at Mount Tai.

523 **Table 3**: Principal component analysis for $PM_{2.5}$ samples.

524 **Table 4**: The $TEF_i$ values of PAHs.

525 **Table 5**: Values of parameters used in the probabilistic cancer risk assessment of PAH

526

527 **Table 1.**Total PAH Concentrations (Mean (Minimum-Maximum), ng $m^{-3}$) at Mount Tai and Other
528 Study sites During the Sampling Period

| Sites | Mount Tai | Mount Tai | Gosan | Mount Lu | YRDNNR |
|---|---|---|---|---|---|
| Years | 2015 | 2010 | 2012 | 2016 | 2014 |
| Sanple | $PM_{2.5}$ | $PM_{2.5}$ | $PM_{2.5}$ | $PM_{10}$ | $PM_{2.5}$ |
| Acy | 0.016(0.006-0.035) | 0.02(0.00-0.05) | NA | 0.97(0.26-6.03) | 0.08 |
| Ace | 0.052(0.008-0.283) | 0.07(0.01-0.16) | NA | 1.04(0.02-6.88) | 0.24 |
| Flo | 0.051(0.003-0.318) | 0.08(0.02-0.18) | 0.004 | 1.27(0.47-5.26) | 2.00 |
| Phe | 0.331(0.004-2.306) | NA | 0.003 | 2.17(0.80-7.67) | 0.69 |
| Ant | 0.046（0.005-0.284） | 0.07（0.00-0.20） | NA | 0.430.02-1.57) | 0.14 |
| Flu | 0.128（0.023-0.469） | 0.98（0.28-2.07） | 0.005 | 1.14(0.28-2.83) | 2.02 |
| Pyr | 0.076(0.014-0.202) | 0.71(0.20-1.49) | 0.005 | 3.19(0.81-11.76) | 1.21 |
| BaA | 0.037(0-0.198) | 0.59(0.10-1.46) | 0.002 | 0.40(0.06-1.56) | 0.13 |
| Chr | 0.076(0.018-0.612) | 0.53(0.15-1.17) | 0.004 | 0.86(0.13-3.17) | 0.07 |
| BkF | 0.062(0.008-0.208) | 0.43(0.12-2.13) | 0.006 | 0.73(0.05-3.22) | 0.20 |
| BbF | 0.092(0-0.306) | 1.62(0.30-3.60) | 0.011 | 1.59(0.25-5.04) | 0.05 |
| BeP | 0.095(0.009-0.800) | NA | 0.006 | NA | NA |
| BaP | 0.040(0-0.114) | 0.44(0.09-1.01) | 0.010 | 0.74(0.14-2.24) | 0.29 |
| DahA | 0.022(0.004-0.216) | 0.10(0.01-0.25) | 0.002 | 0.86(0.14-8.02) | 0.10 |
| IcdP | 0.100(0.010-0.278) | 0.35(0.09-0.72) | 0.010 | 1.34(0.32-9.92) | 0.10 |
| BghiP | 0.096(0.009-0.227) | 0.38(0.08-0.87) | 0.012 | 1.65(0.38-13.39) | 0.12 |
| Cor | 0.041(0.009-0.120 ) | NA | NA | NA | NA |

529 NA-not analyzed.

530

531 **Table 2.** Diagnostic PAH ratios for samples collected at Mount Tai

| Diagnostic ratio | Samples value | Value range | Source assignment |
|---|---|---|---|
| Phe/(Phe + Ant) | 0.88 | < 0.7 | Petrogenic |
| | | > 0.7 | Fossil fuels and lubricant oils |
| Flu/(Flu+ Pyr) | 0.63 | < 0.4 | Unburned petroleum |
| | | 0.4-0.5 | Liquid fossil fuel |
| | | > 0.5 | Wood and coal combustion |
| BaA/(BaA + Chr) | 0.33 | 0.2-0.35 | Coal combustion |
| | | > 0.35 | Vehicular emissions |
| IcdP/(IcdP +BghiP) | 0.51 | < 0.2 | Petrogenic |
| | | 0.2-0.5 | Petroleum combustion |
| | | > 0.5 | Coal, grass, and wood combustion |

532

533 **Table 3.** Principal component analysis for $PM_{2.5}$ samples

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Acy | | | |
| Ace | 0.984 | | |
| Flo | 0.988 | | |
| Phe | 0.982 | | |
| Ant | 0.992 | | |
| Flu | 0.809 | | |
| Pyr | | | 0.661 |
| BaA | | | 0.739 |
| Chr | | 0.876 | |
| BkF | | | 0.902 |
| BbF | | | 0.798 |
| BaP | | 0.955 | |
| BeP | | 0.904 | |
| DahA | | 0.879 | |
| BghiP | | 0.893 | |
| IcdP | | | 0.819 |
| Cor | | | |
| Explained the variance | 31.4% | 30.8% | 24.6% |
| Source | coal combustion | multiple sources | vehicular emission |

534

535

536

537

538 **Table 4.** The $TEF_i$ values of PAHs

| PAH | TEF |
|---|---|
| Ace | 0.001 |
| Acy | 0.001 |
| Flo | 0.001 |
| Phe | 0.001 |
| Ant | 0.01 |
| Flu | 0.001 |
| Pyr | 0.001 |
| BaA | 0.1 |
| Chr | 0.01 |
| BbF | 0.1 |
| BkF | 0.1 |
| BaP | 1 |
| BeP | 0.01 |
| DahA | 1 |
| IcdP | 0.1 |
| BghiP | 0.01 |
| Cor | 0.01 |

539

540

541 **Table 5.** Values of parameters used in the probabilistic cancer risk assessment of PAH.

| Parameters | Meaning | Units | Infants | Children | Adults | References |
|---|---|---|---|---|---|---|
| | Age | Years | 0-1 | 2-18 | 19-70 | |
| BW | Body weight | kg | 9.1±1.25 | 29.70±5.62 | 71.05±13.60 | |
| | Inhalation rate | $m^3 day^{-1}$ | 5.36 | 11.41 | 15.73 | (Hoseini et al., 2016) |
| EF | Exposure frequency | Days $year^{-1}$ | 350 | 350 | 350 | |
| ED | Exposure duration | Year | 0–1 | 0-17 | 0-52 | (Collins et al., 1991) |
| AT | Averaging time | Days | 25550 | 25550 | 25550 | |
| cf | conversion factor | | $10^{-6}$ | $10^{-6}$ | $10^{-6}$ | |
| CSF | cancer slope factor | $(mg\ kg^{-1} day)^{-1}$ | 3.14 | 3.14 | 3.14 | |

542